

Decomposition of Diazoalkanes Induced by Electron Transfer from Fluoren-9-yl Anions

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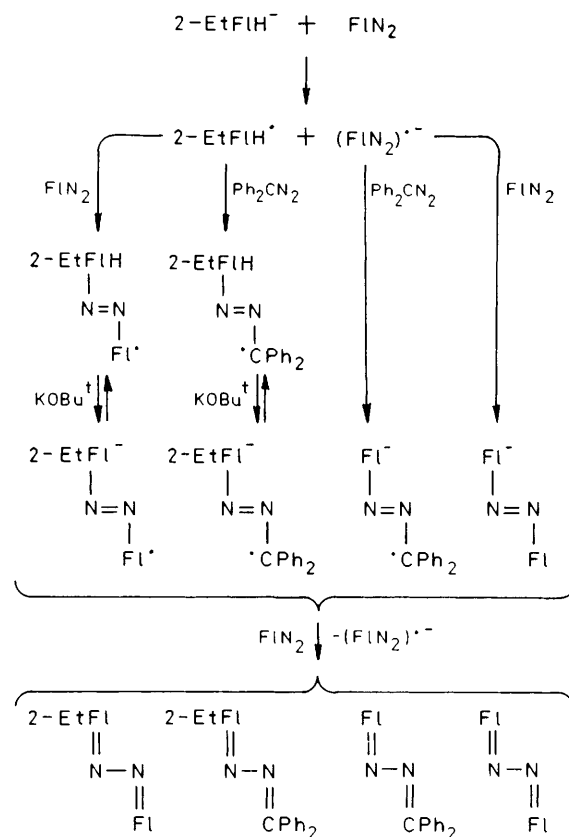
Summary Electron transfer from fluoren-9-yl anions to 9-diazofluorene initiates a dual entry into an anion-radical chain reaction yielding azines which, from ^{15}N -labelling studies, are formed at least in part without intervention of a carbene radical anion.

In 1953 Beringer *et al.*¹ reported that fluoren-9-yl-lithium reacts with 9-diazofluorene (FIN_2) to produce difluoren-9-ylidenehydrazine (= fluorenone azine) which they believed arose by nucleophilic attack of the carbanion on the terminal nitrogen atom of the diazoalkane. This mechanistic suggestion has recently been revived by McDonald and Lin.² We now report experiments carried out under rather different conditions which lead us to doubt this interpretation and which also throw new light on the proposal that one-electron reduction of diazoalkane leads to intermediate formation of a carbene radical anion.³

In a medium consisting of *t*-butyl alcohol–dimethyl sulphoxide (9:1 v/v) containing potassium *t*-butoxide (0.1 M; 1 equiv.), 9-diazofluorene (1 equiv.) slowly decomposes at room temperature yielding difluoren-9-ylidenehydrazine. Addition of fluorene (0.5 equiv.) greatly enhances the rate of the reaction which is complete within a minute. The azine can be isolated in almost 100% yield (based on diazoalkane) and most of the fluorene is also recovered along with small amounts of bifluoren-9-yl and bifluoren-9-ylidene. The yield of nitrogen is only 80–85%, but this is increased to 95% when the amount of fluorene used is decreased by a factor of five. When the reaction is carried out with rigorous exclusion of oxygen, the reaction mixture at the end of the reaction remains dark red in colour and shows strong e.s.r. absorption attributable to difluoren-9-ylidenehydrazine radical anion.

Under these reaction conditions diazodiphenylmethane does not decompose. However, an equimolar mixture of 9-diazofluorene, diazodiphenylmethane, and fluorene readily evolves nitrogen, all of the diazoalkane disappearing together with some of the diazodiphenylmethane. The symmetrical difluoren-9-ylidenehydrazine and the unsymmetrical diphenylmethylene(fluoren-9-ylidene)hydrazine are produced in roughly 50:50 ratio but this changes to 87:13 when the proportion of hydrocarbon 'catalyst' is reduced to a fifth. That the unsymmetrical azine is formed in part from the 'catalyst' is shown by using 2-ethylfluorene which led to the production of four azines, the symmetrical and unsymmetrical ones previously observed together with the corresponding 2-ethyl analogues, in the approximate ratio 40:20:5:35. This finding indicates that azines arise from an intermediate derived from the hydrocarbon which reacts preferentially with diazodiphenylmethane while the intermediate responsible for the formation of the unsubstituted azines favours reaction with diazoalkane. A radical-anion chain process

initiated by electron transfer from the carbanion to 9-diazofluorene is proposed (Scheme). In part, this is analogous to the mechanism previously suggested for the electrochemical reduction of the diazoalkanes.³



SCHEME. Fl = fluoren-9-ylidene

McDonald and Hawley^{2,3} have proposed that the radical anions formed by addition of an electron to 9-diazofluorene and diazodiphenylmethane rapidly lose nitrogen giving the related carbene radical anion ($\text{Ar}_2\text{C}^\bullet$)⁻ which attacks a diazoalkane molecule or abstracts a hydrogen atom from the medium. We have used ^{15}N -labelled 9-diazofluorene, prepared from fluorenone oxime (88% ^{15}N) by reaction with chloramine,⁴ and unlabelled diazodiphenylmethane in conjunction with 2-ethylfluorene and examined the distribution of the label in the difluoren-9-ylidenehydrazine, 2-ethylfluoren-9-ylidene(fluoren-9-ylidene)hydrazine, and diphenylmethylene(fluoren-9-ylidene)hydrazine produced using gas chromatography–mass spectrometry.[†] It was found that both the unsubstituted

[†] 2 m × 0.6 cm column containing 3% OV1 on celite at 250 °C, used in conjunction with a Hewlett Packard Model 5985. Because of the presence of intense $M - 1$ peaks in the mass spectrum, the accuracy of the ^{15}N -analyses is probably no better than ±10% of the stated figure.

and ethyl-substituted difluorene-9-ylidenehydrazines were *ca.* 85% mono-labelled while the unsymmetrical azine contained about 40% of mono-labelled compound. We conclude that part at least of the products from the radical anion chain arise from diazofluorene radical anions which do not lose their nitrogen. However, we do not believe that the presence of unlabelled mixed azine necessarily indicates the participation of carbene radical anions; both diazofluorene radical anion and diazodiphenylmethane are ambident species and the mixed azine could be formed by attack of C-9 of the diazofluorene radical anion on the terminal nitrogen of diazodiphenylmethane with loss of labelled nitrogen.

J.M.B. is on sabbatical leave from the University of Trondheim, supported by generous grants from Norges Almenvitenskapelige Forskningsråd and Norges Teknisk-Naturvitenskapelige Forskningsråd. We are grateful to Mr. K. White, Donnan Laboratories, University of Liverpool for running e.s.r. spectra, and for helpful consultations.

(Received, 28th June 1979; Com. 695.)

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² R. N. McDonald and K.-W. Lin, *J. Amer. Chem. Soc.*, 1978, **100**, 8028.

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⁴ M. O. Forster, *J. Chem. Soc.*, 1915, **107**, 260; J. Meinwald, *J. Amer. Chem. Soc.*, 1960, **82**, 2857; *cf.* D. Bethell and R. McKeivror, *J.C.S. Perkin II*, 1977, 327.